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ASSESSMENT OF ALTERNATIVE PHENOL RECOVERY PROCESSES

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INDUSTRIAL WASTE DIVERSION PROGRAM
FINAL REPORTS # 1

Assessment of Alternative Phenol Recovery Processes

Report prepared for :

Waste Management Branch
Ontario Ministry of the Environment

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ASSESSMENT OF ALTERNATIVE PHENOL RECOVERY PROCESSES

Report prepared for:

Waste Management Branch
Ontario Ministry of the Environment

In consultation with

Zenon Environmental Inc.

Report prepared by:

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DISCLAIMER

This report is in partial fulfillment of conditions of a grant given to CanadianOxy Chemicals Ltd. by the Ministry of the Environment under the Industrial Waste Diversion Program. The report was prepared by Zenon Environmental Inc. for CanadianOxy Chemicals Ltd. and documents results of work for which the Ministry of the Environment provided financial assistance.

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SUMMARY

CanadianOxy Chemicals Ltd. owns and operates a phenol-formaldehyde resin plant in the City of Fort Erie, Ontario. Water is produced as a by-product of the polymerization reaction and is drawn-off the batch reactors in three distinct cuts. About 1,000 gallons of distillate is collected each day generally containing 5 to 8% phenol. The distillate is presently being hauled offsite for disposal at Tricil. In 1987, the total cost of disposal was in the order of $280,000 and the value of lost phenol was about $120,000. CanadianOxy is considering taking measures to recover phenol from the distillate and to treat all effluents on-site to meet sewer discharge limits.

ZENON Environmental Inc. has completed a study for CanadianOxy that focussed on evaluating existing phenol recovery technologies, selecting the most feasible process for the application and confirming the viability of the process with bench-scale testing. Of the seven processes evaluated, resin adsorption with formaldehyde regeneration was the only process found capable of recovering phenol economically at the Fort Erie plant. A bench-scale study confirmed the technical feasibility of the process, and a preliminary economic analysis suggested that a payback period as little as 1.8 years is possible.

Equilibrium adsorption tests were performed on four candidate resins to determine their phenol capacities. The results showed that WA30, a weak base anion resin, had the greatest capacity for phenol followed by XAD7, a slightly polar, non-ionic adsorbent. Column tests were conducted with both resins to evaluate the efficiency of the process. The WA30 resin again showed a greater capacity for adsorbing

phenol (7 bed volumes collected before 90% breakthrough compared to 4 bed volumes for XAD7), but the XAD7 resin was observed to regenerate more efficiently. The breakthrough profiles were obtained for both resins at hydraulic loadings of 2, 4 and 6 BV/h. The WA30 profiles were found to be more significantly affected by increasing hydraulic loadings.

In light of the favourable economics for the recovery process, ZENON recommends that further process development and evaluation be carried out on a pilot-scale.

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1.0 INTRODUCTION

1.1 Background

CanadianOxy Chemicals Ltd. presently operates a phenol-formaldehyde resin plant in the City of Fort Erie, Ontario. The plant produces a total of 12 million pounds per year of moulding compounds, industrial resins and foundry resins.

The process involves a condensation polymerization reaction of phenol and formaldehyde in two batch processing kettles. The resin produced by this process is cooled and flaked on a flaker belt. The flaked product is either sold directly, pulverized and sold, or used inhouse in pulverized form to produce moulding compounds.

Water is produced as a by-product during the polymerization reaction. Water is distilled from each kettle, condensed and collected in a distillate receiver. Throughout a batch operation, the distillate receivers are emptied three times representing three distinct distillate "cuts". The first cut contains about 0.5-1% phenol and the second cut about 2-4% phenol. The third cut is a mixture which separates into two distinct phases, a saturated water phase containing approximately 8% phenol and a heavier organic phase containing about 72% phenol. In all cases, the phenol present in the distillates is primarily the same simple phenol used as raw material for the resin production process. The phenol as generated from the distillate receivers is however, too dilute to be reused directly in the reaction process without first being concentrated.

At the present time, the distillate from both kettles is shipped offsite for disposal at Tricil. In 1987, Tricil hauled and

disposed of approximately 350,000 gallons of distillate (approximately 1,000 gallons per day) along with an additional 44,000 gallons (1,000 gallons per week) of phenol contaminated dyke water containing up to 500 ppm of phenol. The total cost of disposing of this wastewater is in the order of $250,000 to $300,000 per year. In addition, the value of the phenol content in the disposed distillate is about $120,000. Therefore, the potential net saving would be approximately $400,000 per year if all of this phenol could be recovered for reuse and the effluent discharged to the municipal sewer after biotreatment.

In the near future, CanadianOxy plans to convert their existing process to a "low free phenol process" similar to that which has been used in Europe for a number of years. This change will have potentially far ranging and positive environmental benefits to the end users of phenol-formaldehyde resins by significantly reducing the tendency for the resins to release phenol to the environment. However, a disadvantage of the low free phenol process is that it will significantly increase the phenol concentrations in each of the three distillate cuts. Therefore, in order for CanadianOxy to take advantage of low free phenol technology and maintain the plant's operating efficiency, measures will have to be taken to recover and reuse phenol within the plant to the maximum extent possible.

ZENON has completed phase 1 in a project aimed at identifying viable options for recovering phenol at the plant, selecting the best available technology and evaluating the technical and economic feasibility of the process on a bench-scale.

1.2 Objectives

The specific objectives for phase 1 of this project are:

- To carry out a thorough review and assessment of currently available, proven methods for recovering phenols in the concentration ranges present in the recovered distillates.
- To select those processes which are worthy of more detailed technical and economic evaluation.
- To conduct preliminary bench-scale testing to confirm the technical suitability of the phenol recovery process which appears to be best suited to this particular application.
- To perform an economic analysis of the preferred recovery process based on the experimental data obtained in the bench-scale study.
- To provide a workplan and a cost estimate for Phase 2 of the project involving pilot-scale testing and evaluation.

2.0 REVIEW OF PHENOL RECOVERY TECHNOLOGIES

2.1 General

A preliminary review of the literature had produced seven potential phenol recovery methods. Each of these methods will be discussed in some detail and evaluated based on available technical and economic data. The recovery methods being considered are:

1. Resin Adsorption
2. Carbon Adsorption
3. Solvent Extraction
4. Critical Fluid Extraction
5. Steam Stripping
6. Reverse Osmosis
7. Gravity Separation

2.2 Resin Adsorption

Resin adsorption functions according to the same principles associated with carbon adsorption. Adsorption is a surface phenomena whereby physical and chemical forces cause sorption of a solute onto the surface of an adsorbent. In resin adsorption, the adsorption forces are much weaker than in carbon adsorption. This permits resin adsorbents to be chemically regenerated fairly effectively, and provides an opportunity to recover sorbed materials (19).

Resin adsorption has been successfully applied for recovering phenol from aqueous effluents (9, 15, 16, 20). A typical recovery process consists of three steps: adsorption, regeneration with either an organic solvent or strong inorganic base,

and separation of the regenerant from the phenol by distillation. A recovery unit installed at a U.S. phenol manufacturing plant is reported to produce effluents with less than 10 mg/L phenol from feeds ranging from 5 to 15 g/L phenol (12). The recovery process is based on patented Rohm & Haas resin adsorption technology.

In a phenolic resin plant, there is a potential for employing concentrated formaldehyde as a regenerant and recycling the resulting phenol/formaldehyde eluate directly back to the polymerization reactors (13, 15). Fox (1978) reported that a pilot plant obtained effluents with under 25 ppm phenol from a 5% phenolic feed in a single resin bed using 44% formaldehyde as a regenerant. This application requires no distillation train to recover phenol from the regenerant.

Formaldehyde regeneration significantly simplifies the recovery process. Only two streams are generated, the recovered phenol in formaldehyde stream and the aqueous effluent. This effluent will have to be further treated to meet sewer discharge limits.

The recovery process can be adapted to operate continuously by installing two or more columns for simultaneous loading and regeneration. Loading is performed at a space velocity, i.e. volumetric flow rate per volume of adsorbent, dependent on the phenol concentration of the influent, the desired effluent quality and the time required to regenerate the unit.

As in typical ion exchange processes, the loading, regeneration and rinse sequence can be all executed automatically with the appropriate controller, on-line analyzers and control valves.

With formaldehyde regeneration, the capital cost for this recovery process is considerably reduced as there is no need for any distillation units. From cost data in the literature, the total installed equipment cost will be in the order of $200,000 to $300,000 for the capacity range required at the CanadianOxy plant (16). The operating costs also become negligible due to low energy and manpower requirements. The highest operating cost will probably be attributed to resin replacement costs generally amortized over a 5 year period.

2.3 Carbon Adsorption

Activated carbon adsorption is a well developed technology used in a wide range of waste treatment applications. In general, activated carbon absorbs most organic compounds to some extent but is most effective for the least polar and least soluble organic compounds. Carbon adsorption is commonly used in industry to treat waste streams containing phenols below 500 mg/L (17, 23). However, Van Stone reported successful treatment of 1950 mg/L phenol wastewater by activated carbon yielding an effluent phenol level below 0.1 mg/L (32).

Activated carbon can be employed either in a granular or powdered state for wastewater treatment. The use of powdered carbon involves suspension of the carbon in the wastewater in a stirred container and subsequent separation of the carbon/wastewater slurry via a sedimentation process. When granular carbon is used, the carbon is contained in a fixed column or bed through which the wastewater is passed and contacted with the carbon. Despite the lower carbon costs and shorter equilibrating times associated with powdered carbon,

granular carbon applications are by far more common due to the difficulty in separating powdered carbon from the wastewater suspension and the lack of efficient powdered carbon regeneration systems (14).

After the capacity of a carbon bed is exhausted, the carbon has to be removed from the contactor vessel and regenerated. In the regeneration process, adsorbed materials are removed from the carbon porous structure thus reinstituting its ability to adsorb impurities.

Several modes of regeneration can be employed including thermal, steam treatment, solvent extraction, acid or base treatment and chemical oxidation (14). However, only thermal regeneration using a multiple - hearth or rotary - tube furnace is widely applied in wastewater treatment. Thermal regeneration is accomplished by dewatering the carbon and then heating it to a temperature of 815-925oC to volatilize and combust the adsorbed material.

The literature indicates that the use of carbon adsorption is presently restricted to phenol removal applications (14, 23). The process has not been applied to phenol recovery due to the lack of an efficient regeneration system that does not decompose or chemically alter the recovered phenol.

Although carbon adsorption can reduce phenol levels below 0.1 mg/L in the waste effluent, there is no efficient means presently available to remove the adsorbed phenol without decomposing or chemically altering it. Hence, carbon adsorption will not be considered further for this application.

2.4 Solvent Extraction

Solvent extraction is presently the most widespread method used to recover phenol in resin manufacturing plants. Several processes are available commercially and have established their viability in the field (31). All the processes basically involve phase separation, solvent extraction using a specialized extraction column and distillation to recover the solvent and purify the aqueous effluent to meet discharge limits. The literature on two established processes was examined in some detail.

Chem-Pro Corp. of Fairfield, N.J. has successfully developed an extraction process for phenol recovery (21). A proprietary solvent in a packaged extraction - distillation system can be used to recover phenol and cresols from a wide range of aqueous wastes. Extraction is performed in a Karr Reciprocating Plate Extractor. The dephenolized raffinate taken off the bottom of the extraction column is sent to a stripper to remove traces of solvent before discharging the water to the sewer. The phenol-rich extract from the top of the column is distilled to produce 99 + % phenol and recycled solvent. The process is reported to handle incoming phenol concentrations from a few parts per million to saturation (approximately 8%). Aqueous effluents containing 1 ppm phenol and 1 ppm extracting solvent are achieved.

The General Electric Company of Pittsfield, Massachusetts reported of a phenol recovery process which uses a counter-current reciprocating plate extraction column manufactured by Chem-Pro Corp. and a distillation column (24). Isobutyl acetate was used as the solvent since it has a favorable solubility for phenol, it is

biologically treatable, and it does not adversely affect the phenol/aldehyde reaction. The process is similar to the Chem-Pro process described above except that no stripper is employed to purify the raffinate stream. The raffinate consists of water with 0.1 - 0.3% phenol and 0.6% acetate (solubility in water) and is discharged to a municipal wastewater treatment plant. The phenol/solvent extract is separated in a multi-step distillation process.

In an extraction process, design and operating parameters can be modified to optimize the phenol recovery process to a specific waste stream. The design parameters include the physical column dimensions, number of plates and stages, inter-plate distance and solvent type. Some of the operating parameters to be considered are the magnitude of the shaft displacement, stroke speed of the shaft and feed and draw-off rates. Also, the problem of solvent loss due to slight solubility in wastewater verses efficiency of phenol removal must be balanced economically, as solvent costs can be high (23).

The solvent extraction process is capable of handling a wide range of influent phenol concentrations effectively. The recovered phenol can be purified in excess of 99% in a well-designed phenol/solvent distillation column. The dephenolized effluent must be stripped of residual phenol and solvent before meeting municipal sewer discharge regulations. A non-regenerating adsorption system may be considered as an alternative to a stripper.

Though phenol recovery by solvent extraction is technically a very attractive process, its economic feasibility is generally limited to capacities of 5 USGPM or greater due to the high capital and

operating costs involved. For a capacity range under 5 GPM, solvent extraction would require a capital investment much greater than $500,000 for this application (33).

2.5 Critical Fluid Extraction

In critical fluid extraction, a specific organic compound is removed from an aqueous medium by dissolving the organic in a critical fluid. Such a fluid exists at or near its critical point where it exhibits properties of both a liquid and a gas. The critical fluid behaves like a liquid organic solvent in that it can dissolve significant amounts of organic substances, but also behaves like a gas in that its extraction rate is much higher than for a typical liquid solvent (7, 8).

Several different types of gases have been used for critical and super critical extractions (eg. carbon dioxide, propane, ethylene and ammonia). Carbon dioxide has become the most popular critical fluid solvent since it is inexpensive, non-toxic and has no residual effect on the organic product. The critical point of carbon dioxide is reached at 31oC and 72.9 atms.

In the critical fluid extraction process for phenol recovery, the liquid waste is fed to the top of an extractor operating at a critical pressure and temperature of carbon dioxide. Carbon dioxide is condensed by compression to the required critical pressure and injected at the bottom of the extractor. The solvent fluid flows upwards, contacting the liquid waste and dissolving out the phenol. A separation of 99% or greater is usually possible. The mixture of

solvent gas and dissolved phenol is removed from the top of the column while clean water leaves through the bottom. The extract is sent to a second column where the temperature and pressure are dropped causing the phenol to separate from the solvent. Concentrated phenol is recovered from the bottom of the separator while the solvent is recycled to the extractor after being recompressed.

Commercial processing units with capacities ranging from 5 - 100 gpm are marketed for this application by Critical Fluid Systems, Inc. of Cambridge, Mass. The units are skid-mounted and constructed of carbon steel or stainless.

CFS systems can be designed to achieve final concentrations as low as 100 ppb or less. The guideline limit set by the Ministry of the Environment for phenol in water discharged into the natural environment is 20 ppb.

In any extraction process, solvent losses from the system has to be considered. Critical fluid extraction technology has an advantage over other extraction technologies in that it achieves a better separation of the solvent from the extract. This results in smaller solvent losses.

Due to the high operating temperatures and pressures, the equipment and installation costs for the process are fairly high, about the same as distillation processes and twice that of a carbon adsorption system (7). However, operating costs are much lower than distillation and carbon adsorption processes. Equipment and installation costs for a 5 US GPM system were estimated at about US $1 million (34). Due to the high capital costs and relative complexity of

the process equipment, this technology has been eliminated as a potential phenol recovery process for this application.

2.6 Steam Stripping

Steam stripping is essentially a fractional distillation of volatile compounds from a wastewater stream. The process has been applied for phenol removal from effluent streams in phenol manufacturing plants and in the petroleum industry (29).

Steam stripping is generally carried out in a packed tower or conventional fractional distillation column with more than one stage of vapour/liquid contact. Preheated wastewater is introduced near the top of the column and flows counter-current to the steam rising from the bottom of the column. The concentration of the volatile component in the liquid progressively decreases as the liquid passes down through the column. Steam exiting the column is condensed and must be further processed for product recovery. Heat recovered from the wastewater discharged at the bottom of the column is used to preheat the incoming feed.

Phenol has a boiling point of 182oC and vapour-liquid equilibria for a phenol-water system does not allow for much concentration of the phenol wastewater (i.e. the level of removal is limited by the low volatility of phenol). The maximum theoretical concentration of phenol that can be attained in the recovered phenol stream is the solubility of phenol in water under the operating temperature and pressure conditions. It is therefore evident that steam stripping can not be applied to phenol recovery from relatively

concentrated wastewaters.

Both energy requirements and capital costs are prohibitively high for steam stripping. The energy requirements also increases for lower phenol concentrations in the effluent streams. The high capital cost restricts the economical operation to very large capacities, far beyond the range being considered in this application.

2.7 Reverse Osmosis

Reverse osmosis is a salt removal process which has been intensively developed over the past 15 years for treatment of both brackish water supplies and wastewaters. The membrane process involves the passage of water through a semi-permeable membrane under a pressure driving force sufficient to overcome the osmotic pressure of the solute and obtain reasonable production rates of purified water. The reject stream is concentrated in solute.

The most extensive use of RO to date has been in the demineralization of brackish and seawater. However, its application to wastewater treatment is growing with continuing developments being made in membrane chemistry that are reducing fouling tendencies and making membranes more inert (2).

In general, low molecular weight, water soluble organics are poorly rejected by existing reverse osmosis membranes. Phenol also exerts a relatively high osmotic pressure (4). This restricts the degree of concentration than can be practically obtained (i.e. without exceeding feed pressures greater than 1,000 psi). In light of this, reverse osmosis will not be considered as an eligible process for this

application. However, it may be feasible to employ reverse osmosis for concentrating dyke waters prior to a recovery process.

2.8 Gravity Separation

Gravity separation is a physical process whereby suspended solids or a denser liquid phase is separated from an aqueous phase as a result of gravitational forces. Essentially, the technique consists of providing sufficient time and quiescent conditions to allow the denser phase to settle to the bottom of the separation tank. The process may be batch or continuous.

General Electric has a patented separation process based on phenol-water phase equilibria (24). Phenol and water will undergo a two-liquid phase separation only within certain limits of temperature, pH and phenol concentration. Operating temperature ranges from 30-45°C with a phenol concentration range of 25-40% by weight in water.

The third cut of distillate from the phenol-formaldehyde polymerization reaction consists of a phenol saturated aqueous phase (about 8% phenol) and a water saturated organic phase (about 72% phenol). Gravity separation can be effectively used to recover the phenol rich organic phase. This supporting process will be useful in lowering the cumulative concentration of the three distillate cuts and thereby reducing the loading rate in the recovery process.

A gravity separation process is easy to operate and requires low capital investment. Very little energy is consumed, and the required equipment is relatively simple and commercially available. It

has a potential for reducing operating costs upstream in the main recovery process.

3.0 PROCESS SELECTION

3.1 Selection Criteria

The seven candidate phenol recovery processes were evaluated and compared on the basis of the following criteria (listed in descending order of priority):

1. **Technical Feasibility** - Is the process capable of producing a recovered phenol stream suitable for recycle and an aqueous effluent sufficiently low in residual phenol?
2. **Economic Feasibility** - Can the process possibly achieve a return on investment of 20% or better and a maximum payback period of three years or less?
3. **Safety** - Does the process pose minimum risk to operating personnel in the plant under normal and upset operating conditions?
4. **Ease of Operation** - Is the process simple enough to require minimal operator attention and onsite technical support?
5. **Reliability** - Is the process capable of performing reliably in a plant setting with minimal operator involvement?
6. **Flexibility** - Can the process effectively recover phenol over a wide range of influent phenol concentrations?
7. **Future Expansion** - Can the process be easily adapted to handle capacities greater than the design capacity?
8. **By-product Disposal** - Does the process produce a by-product stream that can not be treated onsite?

3.2 Techno-economic Justification of Selected Process

Table 3.1 summarizes the evaluations done on the seven alternative phenol recovery processes reviewed in section 2. The processes were evaluated based on the criteria outlined in section 3.1.

Resin adsorption was the only process that met all the established criteria. Solvent extraction and critical fluid extraction were the only other two processes found capable of recovering phenol sufficiently concentrated for direct recycle to the batch reactors. However, both of these extraction processes had to be dismissed from further consideration as they are unable to recover phenol economically in the capacity range being investigated for the CanadianOxy operation. On the other hand, the capital investment for resin adsorption with formaldehyde regeneration stays proportional to feed rate in this capacity range and, as a result, the process can potentially meet the economic feasibility criteria established in section 3.1. The remaining processes were not found to be technically feasible in this application.

Resin adsorption was therefore selected as the best available technology for recovering phenol at the CanadianOxy plant. The rest of this report will centre on a bench-scale evaluation and a preliminary economic assessment of this process.

Gravity separation was considered only as a pretreatment method to reduce the amount of phenol to be removed in the recovery process. This process already occurs to some degree in the distillat receivers with the separation of the aqueous and phenol-rich organic

Table 3.1 - Summary of Process Evaluations

Process	Technical Feasibility	Economic Feasibility	Safety	Ease of Operation	Reliability	Flexibility	Future Expansion	By-product Disposal
1. Resin Adsorption	Yes	Yes	Yes	Yes	Yes	Yes	Yes	No
2. Carbon Adsorption *	No	No	-	-	-	-	-	-
3. Solvent Extraction	Yes	No	Yes	No	Yes	No	No	Yes
4. C. F. Extraction	Yes	No	Yes	No	No	No	No	No
5. Steam Stripping *	No	No	-	-	-	-	-	-
6. Reverse Osmosis *	No	No	-	-	-	-	-	-
7. Gravity Separation **	Yes	Yes	Yes	Yes	Yes	Yes	Yes	No

* Not fully evaluated as the process was not found to be technically or economically feasible.

** Evaluated as a supporting process.

layers. Optimization of temperature and pH conditions in the receivers may be considered in the second phase of the project.

3.3 Design Considerations for Selected Process

3.3.1 Process Description

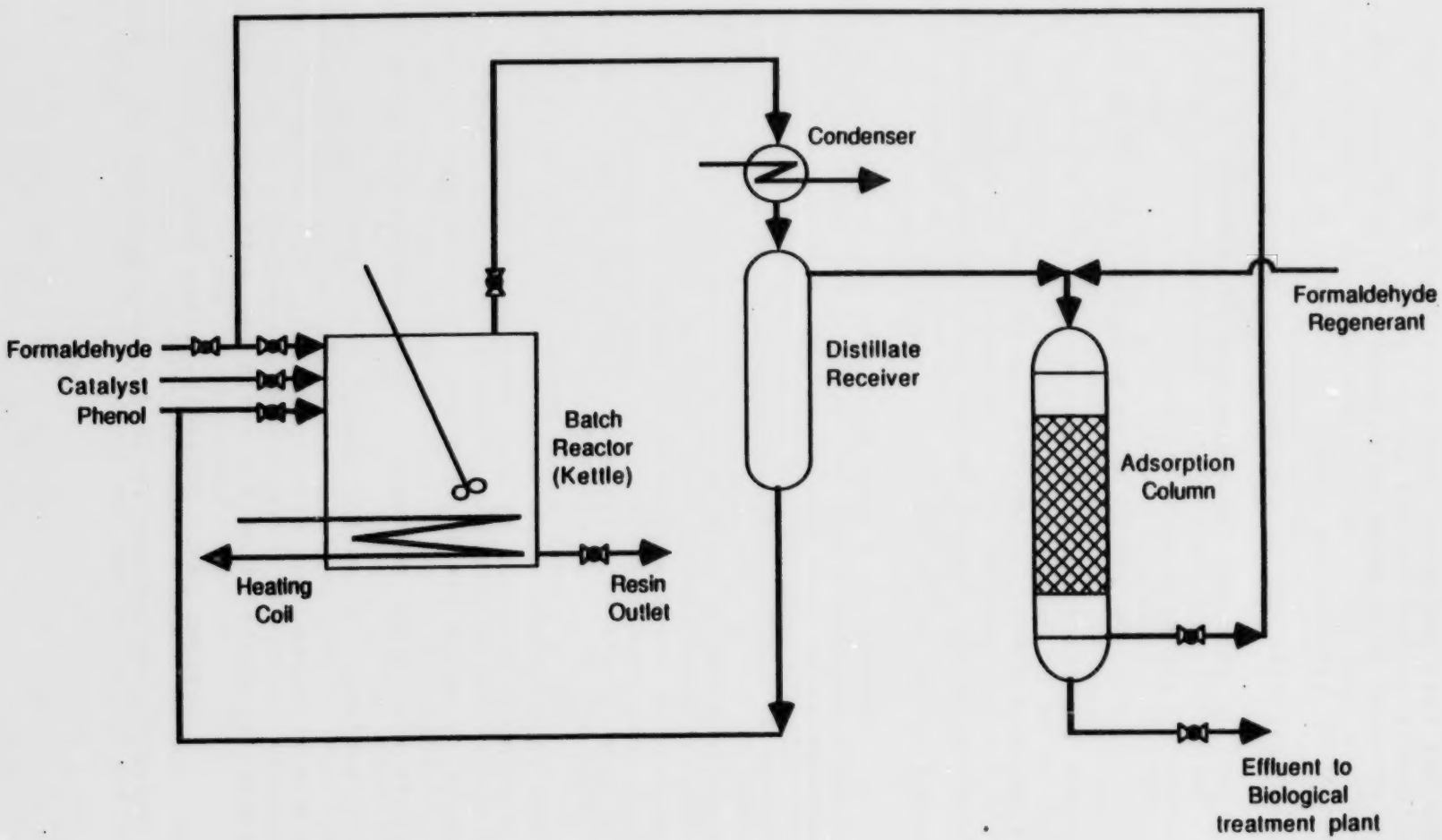
Figure 3.1 shows a simplified flow diagram of a proposed phenol recovery process for the CanadianOxy phenol-formaldehyde plant in Fort Erie. Water vapour drawn off the batch reactor during the phenol-formaldehyde polymerization reaction is condensed and collected in a distillate receiver. The distillate also contains some phenol stripped from the liquid mass in the reactor. In the third distillate cut, phenol concentration in the distillate exceeds its solubility (approx. 8%), and an organic phase containing about 72% phenol settles to the bottom of the receivers. This phenol rich phase will be taken off the bottom of the receiver and recycled back to the reactor after some intermediate storage.

The aqueous phase of the distillate (containing < 8%) will be pumped from the receiver to the top of the adsorption column. The treated effluent will be sent to a biological treatment plant for further treatment prior to discharge to a municipal sewer. Once the capacity of the resin adsorption bed is exhausted, the column will be regenerated with formaldehyde solution. The eluant containing 10-20% phenol is recycled back as a feed to the reactor.

3.3.2 Resin Adsorption

Phenol is removed with macroreticular adsorbent resins by physical adsorption. In general, non-polar or hydrophobic solutes are

Figure 3.1 - Flow Diagram of Resin Adsorption Process



adsorbed onto non-polar adsorbents while polar or hydrophilic solutes are adsorbed onto polar adsorbents. Organic compounds such as phenol consist of hydrocarbon chains or rings with polar functional groups. These molecules can be thought of as having both hydrophobic and hydrophilic ends and therefore can be adsorbed onto either polar or non-polar polymeric adsorbents.

For the phenol to be adsorbed, the affinity of the resin surface for phenol must be greater than the solvating forces exerted by the aqueous phase. Likewise, for elution of adsorbed phenol, the solvating forces exerted by the formaldehyde solution must overcome the attractive forces of the resin adsorbent.

Phenol is a weak acid with a pKa of 9.89 at 20°C. It can therefore exist in a purely undissociated state at one extreme (usually below pH 2) and fully dissociated at a pH above its pKa value. Hence, the performance of an adsorbent of a particular polarity will be dependent on the distribution of dissociated and undissociated phenol molecules in the distillate or effectively the pH of the distillate.

Being a weak acid, phenol can also be removed effectively from aqueous solution by weak base anion exchange resins. The adsorption mechanism in this case involves some ion exchange as well as surface adsorption phenomena. As a result, the capacity of weak base anion exchange resins for phenol are significantly higher than for resin adsorbents, but correspondingly, the phenol can not be as efficiently eluted from the resin bed with organic solvents.

Besides resin polarity, other factors have to be considered in selecting an optimum resin for this application. These factors

include surface area, pore size, chemical and structural stability, and hydraulic characteristics for column operation. The cost of the resin must also be considered in the selection process.

3.3.3 Column Operation

Resin adsorption processes traditionally employ fixed resin beds with either countercurrent or cocurrent regeneration. The operation is typically semi-continuous in that the resin bed has to be regenerated intermittently, but continuous operation is maintained by alternating between two or more columns. The columns for a fixed bed process can be designed and constructed easily and fairly inexpensively.

A modified fixed bed process for resin adsorption was also considered for this application. Reciprocating flow (Recoflo) column technology was commercialized in 1971 by Eco-Tec Ltd. of Pickering, Ontario. The column dynamics involved in this technology is easily adapted to adsorption processes and offers several advantages over a traditional fixed resin bed. The key difference is in the reduced height of the Recoflo column. In a normal fixed bed column, there is a narrow band of resin in which adsorption is taking place. This band moves downwards through the column leaving a layer of exhausted resin above it. A Recoflo column is sized only slightly longer than this adsorption band minimizing the amount of inactive resin. The feed and regenerant distributors are specially designed to prevent channelling and ensure the full bed volume is contacted.

There are several benefits in using a short column. The smaller bed volume and greater extent of bed contact allow for higher

feed flow rates and consequently, shorter cycle times. Regeneration takes only a few minutes compared to a few hours in normal fixed bed columns. The short cycle time sometimes renders a back-up column unnecessary. Other benefits may include reduced equipment costs, longer resin life, lower resin replacement costs, less regenerant requirements and lower space requirements.

Short-cycle operation requires an accurate on-line analysis of phenol concentrations in the column effluents. This may be one significant drawback to using reciprocating flow technology since there is no relatively inexpensive method of measuring phenol concentrations on-line. The advantages and disadvantages associated with reciprocating flow technology and a traditional fixed bed operation will have to be considered in more detail in a pilot-scale study.

4.0 BENCH-SCALE EVALUATION

4.1 Objectives

A bench-scale study of the phenol recovery resin adsorption process was conducted to establish its technical viability and to obtain operating data for costing a full-scale system. More specific objectives of this bench-scale study are given below:

- Determine the equilibrium uptake capacities of commercially available adsorbent resins at varying distillate phenol concentrations in order to select the two best resins for this application.
- Perform adsorption and regeneration column tests to further screen the candidate resins and select the best performing resin.
- Conduct further column tests with the selected resin to determine the optimum hydraulic loading.
- Estimate the degree of phenol concentration and effluent quality that can be achieved from breakthrough profiles observed in column tests.
- Based on experimental data, make preliminary calculations to size the full-scale system and estimate service and regeneration times per operating cycle.

4.2 Experimental Procedures

4.2.1 Equilibrium Adsorption Tests

Equilibrium adsorption tests were performed to determine the total capacity of polymeric adsorbents for phenol adsorption in

Table 4.1 - Characteristics of Candidate Resins

Resin Type	Chemical Nature	Polarity	Specific Surface Area (m2/g)	Shipping Density (g/L)	True Wet Density (g/L)	Nominal Mesh Size
Amberlite XAD-4	Polystyrene	Non-polar	725	704	1020	20 - 60
Amberlite XAD-7	Acrylic ester	Slightly polar	450	656	1050	20 - 60
Diaion HP20	Polystyrene	Non-polar	718	-	-	40 - 50
Diaion WA30	Polystyrene	Polar	-	620*	1050	16 - 50

* Free base form

equilibrium with varying phenol concentrations. Table 4.1 gives the general characteristics of the resins that were investigated.

60 mL portions of Rohm and Haas XAD4 and XAD7 and Dianex WA30 and HP20 resins were rinsed thoroughly with deionized water and dried in an oven at 105oC. Measured volumes of the dried resins were placed into twenty 250 mL amber coloured borosilicate glass bottles followed by 100 mL of diluted phenol distillate. The volumes of dried resin and distillate dilution factors used for each resin type are shown in Table 4.2. An experimental control was also prepared with 100 mL of undiluted distillate with no resin added.

The neck threads of all the sample bottles were then wrapped with teflon tape to prevent leaking before capping the bottles with metal foil lined caps. All twenty-one sample bottles were then placed on a bottle tumbler rotating at 12 revolutions per minute.

After four to six days of mixing, the bottles were removed from the tumbler assembly and the contents allowed to settle for at least two hours. The distillate samples were then filtered and analyzed for pH and phenol content as described in section 4.2.3. Samples not analyzed for phenol immediately were acidified with phosphoric acid to a pH below 4. This preserves the samples for phenol analysis by preventing phenol decomposition by bacterial action, oxidation and/or reduction.

Two sets of equilibrium tests were done with Dianex WA30, a weak base anion exchange resin. In the first test, the resin was used in its original free base form. In a second test, the resin was first converted to its sulphate form by soaking 60 mL of the resin in 250 mL

Table 4.2 - Sample Preparation for Equilibrium Tests

Sample #	Resin Volume (mL)	Distillate Dilution Factor
1	5	1
2	10	1
3	10	2
4	10	4
5	10	10

of 1M sulphuric acid for 24 hours with occasional mixing. The resin was then rinsed, dried and prepared for testing as outlined above.

4.2.2 Column Tests

Figure 4.1 illustrates the apparatus used for bench-scale column testing. Each test column was made of glass and had an inner diameter of 2.5 cm and an effective depth of 30 cm. A twin head peristaltic pump allowed two test columns to be operated simultaneously under the same feed conditions.

Resins were first rinsed and soaked in deionized (DI) water overnight. The required volume of resin was then charged into the column as a slurry to minimize the amount of air bubbles being trapped in the bed. The bed was then backwashed to remove any trapped air and ensure the bed was well settled.

Before starting each test, sufficient amounts of distillate, eluant and deionized water were added to the three 1L glass beakers. The column was operated in a three step cycle with the suction line to the pump being transferred to either the distillate, eluant or rinse water beakers between steps. The operating sequence was as follows:

Step 1. Phenol adsorption from distillate feed.

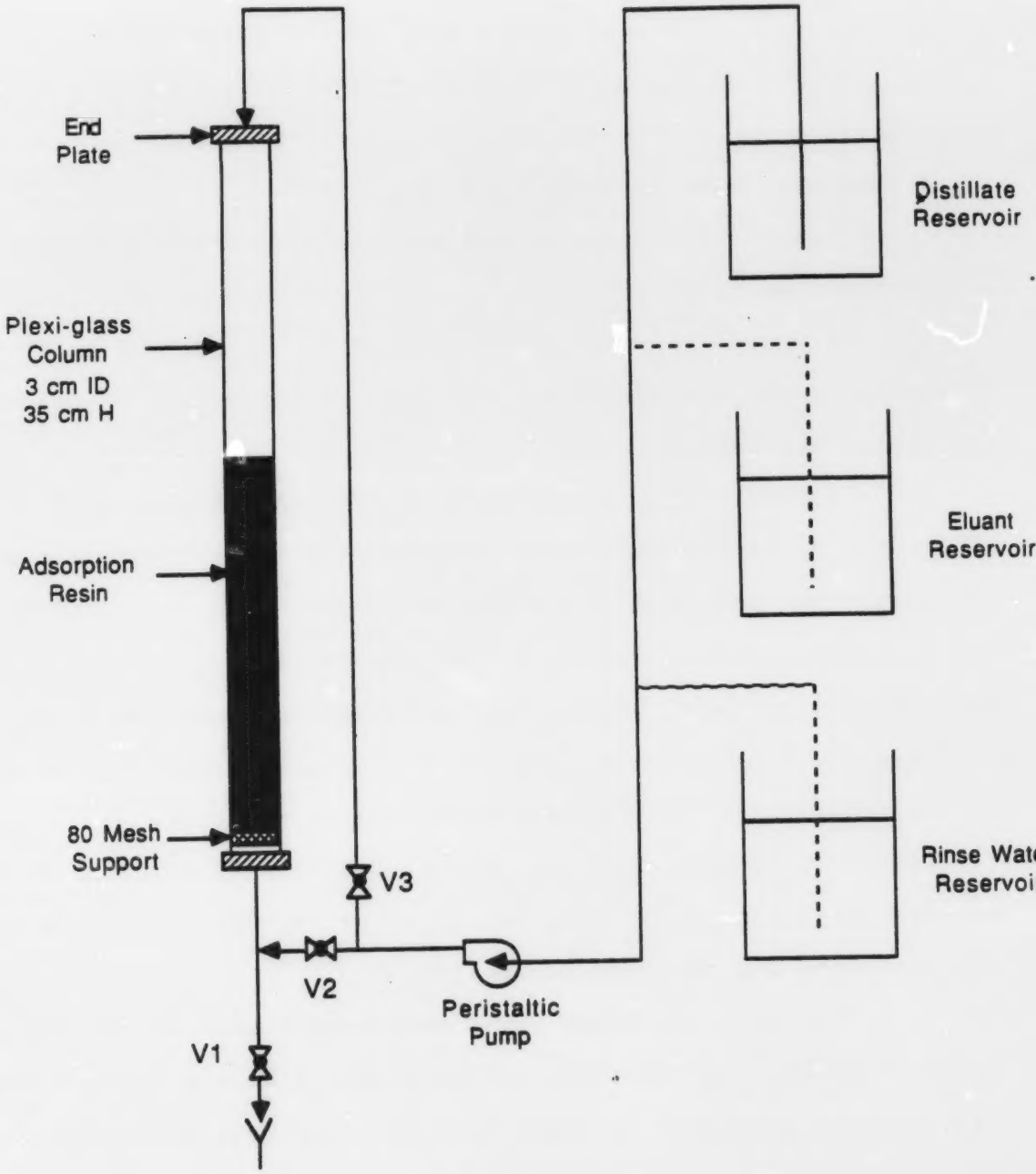
Step 2. Elution with 40% formaldehyde solution.

Step 3. Displacement of eluant void with 10 BV of DI water.

Required flow rates were obtained by adjusting both the valve on the effluent line and the pump controller.

Two sets of column tests were conducted. In the first set of tests (test #1), the two best resins chosen from the equilibrium tests were further evaluated in order to select the most efficient

Figure 4.1 - Apparatus for Bench-scale Column Tests



resin. Two test columns were operated simultaneously using distillate and formaldehyde samples received on November 23rd. The formaldehyde was diluted to 40% before use as an eluant. Table 4.3 gives the operating conditions under which test #1 was performed. The first and second halves of the treated and regeneration effluents were collected separately and analyzed for phenol.

In the second set of tests (#2 to #4), breakthrough profiles were obtained for the WA30 and XAD7 resins at hydraulic loadings of 2, 4 and 6 BV/h. A regeneration profile was also obtained for each resin at 2 BV/h. Refer to Table 4.3 for the operating conditions used in tests #2 to #4. Distillate effluent samples were taken after every bed volume collected until the total capacity of the bed was virtually exhausted. Regeneration effluent samples were similarly taken after every half bed volume collected until most of the adsorbed phenol was eluted from the bed. All the samples were analyzed for phenol immediately after they were collected.

4.2.3 Analytical Procedures

The first distillate sample received on September 14th was analyzed for its metal and anion content by inductively coupled argon plasma (ICAP) emission spectrometry and ion chromatography (IC) respectively. The total organic carbon (TOC) and total phenolics concentrations were also measured. A total chromatographable organics analysis was additionally performed to determine the amount of phenolics other than simple phenol present in the sample.

A sample of dyke water was also analyzed for TOC and total phenolics. This sample was collected on September 14th as well.

Table 4.3 - Operating Conditions for Column Tests

Test#	Bed Depth (cm)	Bed Volume (mL)	Distillate Flow Rate (BV/h)*	Distillate Throughput (BV)	Eluant Flow Rate (BV/h)	Eluant Throughput (BV)
1	10	49	2	4	2	2
2	15	74	2	9	-	-
3	25	123	4	13	-	-
4	15	74	6	12	2	4

* BV: Bed Volume

Samples taken from the adsorption equilibrium tests and the column tests were all tested for total phenolics. Total phenolics determinations were performed based on the 4 - aminoantipyrine colorimetric method (1). Phenol standards of 1, 3, 5 and 10 mg/L and a blank were prepared for constructing a calibration curve. In the analytical procedure,ammonium hydroxide was added to 100 mL of each sample until its pH was greater than 9. The pH of the samples was then adjusted with phosphate buffer to pH 7.9 $\pm$ 0.1. 4-aminoantipyrine and potassium ferricyanide were added and the absorbance of the samples and standards measured against the blank at 500 mm with a Bausch and Lomb Spectronic 70.

4.3 Results and Discussion

4.3.1 Distillate Characterization

Table 4.4 gives the analytical results obtained for three distillate samples and a dyke water sample. The total phenolic concentration of the dyke water is too low to be considered for phenol recovery, and therefore this stream will not be discussed further.

A metal and anion scan on the Sept. 14 distillate sample showed significant levels of sodium, sulphur and sulphate. Sulphuric acid is used as a catalyst in the phenol-formaldehyde polymerization reaction and is likely the source of the sulphur and sulphate concentrations reported. Note that the measured sulphur concentration is in a proportion to the amount of sulphate present that indicates all the sulphur exists in solution as sulphate.

Sodium concentrations at the level being observed is not

Table 4.4 - Sample Characterization

Parameter (mg/L)	Dyke Water Sept. 14	Distillate Sept. 14	Distillate Sept. 29	Distillate Nov. 24
pH	7	7.1	3.7	7.9
TOC	65	63,000	-	-
Total Phenols	300	72,000	90,000	64,000
Fluoride	-	<5	-	-
Chloride	-	<10	-	-
Nitrite (as N)	-	<10	-	-
Bromide	-	<40	-	-
Nitrate (as N)	-	<10	-	-
Phosphate (as P)	-	<40	-	-
Sulphate	-	900	-	-
Calcium	-	12	-	-
Magnesium	-	0.63	-	-
Sodium	-	760	-	-
Potassium	-	<6	-	-
Aluminum	-	15	-	-
Barium	-	<0.02	-	-
Beryllium	-	<0.01	-	-
Boron	-	2.1	-	-
Cadmium	-	<0.02	-	-
Chromium	-	0.35	-	-
Cobalt	-	<0.05	-	-
Copper	-	0.35	-	-
Iron	-	1.4	-	-
Lead	-	<0.2	-	-
Manganese	-	0.98	-	-
Molybdenum	-	<0.2	-	-
Nickel	-	0.18	-	-
Phosphorous	-	1.3	-	-
Silicon	-	4.2	-	-
Silver	-	<0.1	-	-
Strontium	-	<0.01	-	-
Sulphur	-	320	-	-
Thallium	-	<0.5	-	-
Titanium	-	0.11	-	-
Vanadium	-	<0.2	-	-
Zinc	-	0.39	-	-
Zirconium	-	<0.1	-	-

unusual. Sodium hydroxide is added to the sealwater system to prevent corrosion of the vacuum pump that draws off reactor vapours. Some leakage of the sealwater occurs explaining the sodium level being reported. Caustic is occasionally used for cleaning the kettles, and the wastewater is sent to the distillate receivers.

In the three distillate samples received, the pH ranged from 3.7 to 7.9. Distillate pH values at the Fort Erie plant are normally in the 6 to 8 range. The pH of the distillate dictates the extent of phenol dissociation in solution and affects the performance of any resin adsorbent used to remove phenol.

Total phenolic concentrations of the three distillate samples ranged from 6.4 to 8.8%. These values represent the phenol concentration in the receivers at the time of sampling. The three distillate cuts are usually accumulated in the distillate receiver resulting in the formation of an aqueous and organic layer.

The total chromatographable organics analysis performed on the Sept. 14 distillate sample showed only one distinct peak representing simple phenol. The results indicate that the organic content of the distillate consists of greater than 95% of simple phenol.

4.3.2 Equilibrium Adsorption Tests

Equilibrium adsorption tests were done with the September 29 and November 24 distillate samples. The results of these tests are presented in figures 4.2 to 4.5. Experimental data for all the tests are given in Appendix I.

The first set of equilibrium tests were conducted with the

Sept. 29 distillate sample (pH = 3.7). The tests were designed to cover the whole range of phenol concentrations that might contact the resins in a full-scale column. It is assumed that the adsorption process had reached equilibrium after 4 days of contact between the resins and the distillate samples. Thus, the adsorption isotherms obtained represent the equilibrium capacity of each resin at the corresponding equilibrium concentration.

From figure 4.2, it is apparent that the WA30 resin has the greatest capacity for phenol. This was expected since both surface adsorption and ion exchange take place with a weak base anion exchanger. However, the high sulphate concentration (approximately 1,000 ppm) in the distillate causes some poisoning of the WA30 resin which will adversely affect resin capacity in a continuous column operation.

The XAD7 resin had the next highest capacity. Being a non-ionic adsorbent with intermediate polarity, this resin possesses both hydrophobic and hydrophilic surfaces and therefore, will adsorb either the hydrophobic or hydrophilic ends of the phenol molecule. The XAD4 and HP20 resins, on the other hand, are non-polar adsorbents and thus only adsorb the hydrophobic ends of the phenol molecule. These non-polar adsorbents did not perform as well as the XAD7 resin.

The WA30 and XAD7 isotherms show inflection points rather than leveling off with increasing equilibrium concentration. This behaviour usually indicates that a different mechanism of adsorption has become predominant and resulted in increased resin capacity. For the WA30 resin, ion exchange probably becomes the main adsorption

Figure 4.2 - Equilibrium Isotherms (pH 3.7)

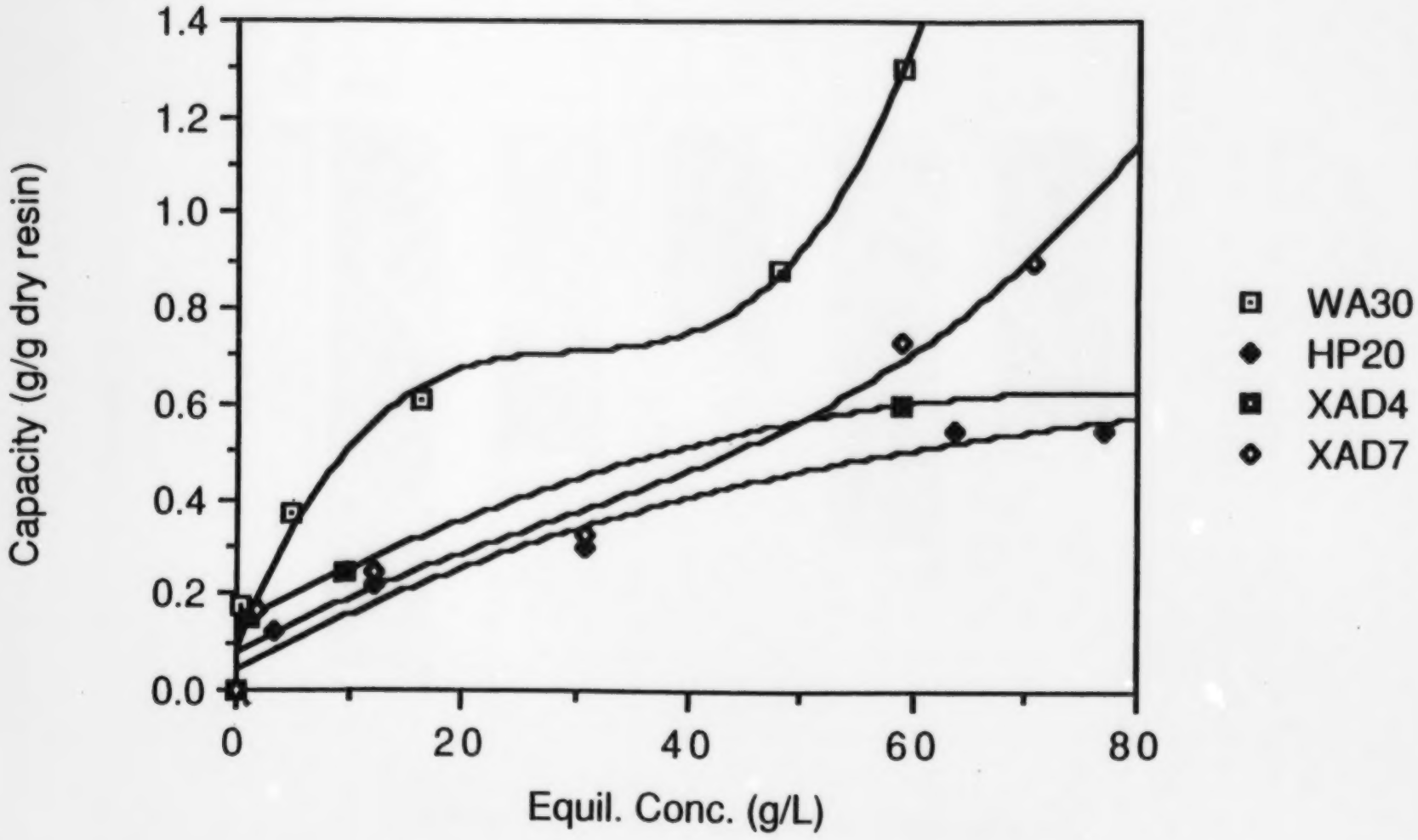
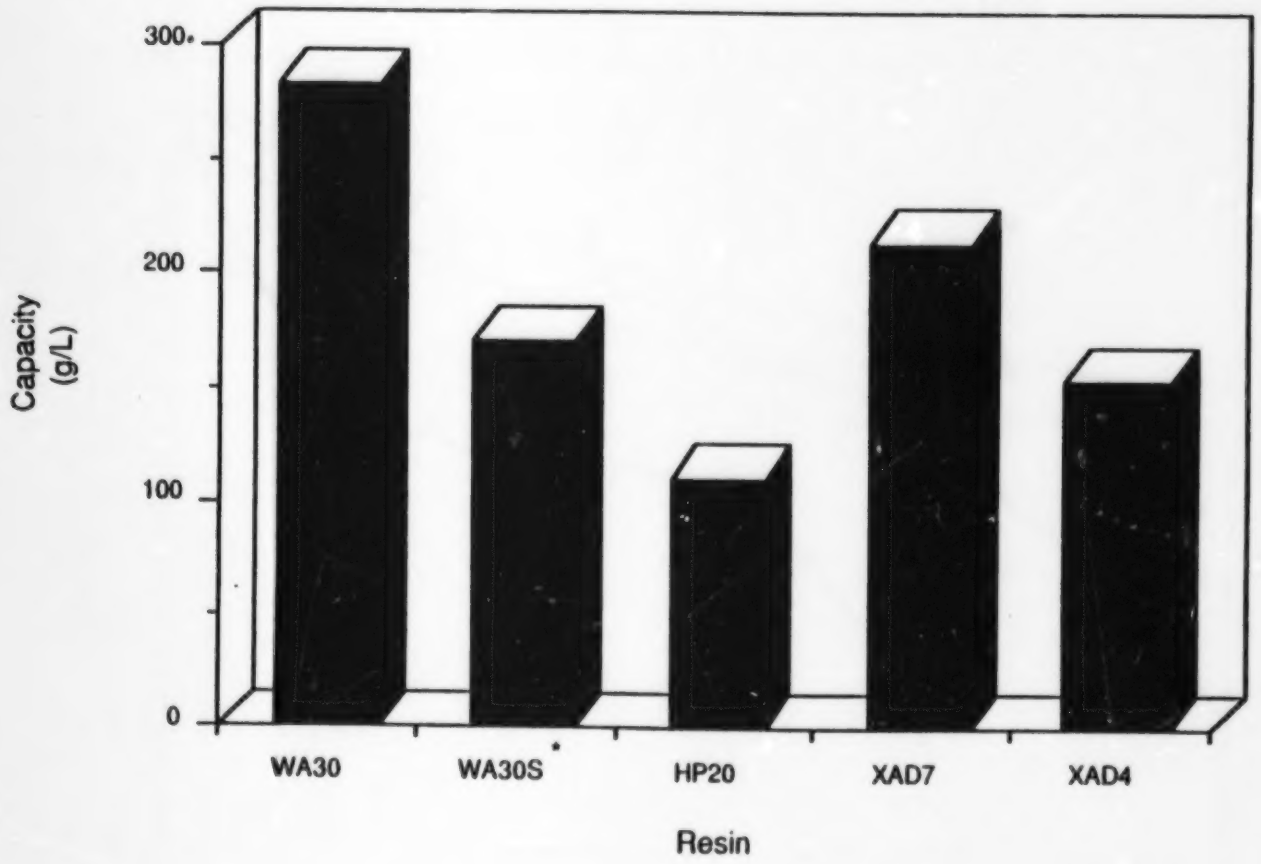


Figure 4.3 - Resin Equilibrium Capacities



* WA30S = WA30 converted to SO4 form

mechanism at higher equilibrium concentrations. The XAD7 resin adsorbs phenol onto either hydrophobic or hydrophilic sites at rates that depend on concentration and pH.

The Nov. 24 distillate sample having a pH of 7.9 was used in the second set of equilibrium tests. 10 mL portions of each resin were contacted with 100 mL of distillate over a 4 day period. Figure 4.3 compares the resin capacities obtained under these conditions. In order to determine the potential effect of sulphate poisoning on the WA30 resin capacity after long-term column operation, some of the WA30 resin was completely converted to its sulphate form and tested separately from the WA30 in its free base form.

Again, the WA30 resin in its free base form exhibited the greatest capacity for phenol. In its sulphate form, the WA30 resin still performed reasonably well. Based on these results, the WA30 and XAD7 resins were selected for further evaluation in a column operation.

Complete isotherms were constructed for the WA30 (sulphate form) and XAD4 resins and compared with the isotherms obtained with the Sept. 29 distillate sample in figures 4.4 and 4.5. The reduced performance of the WA30 with the Nov. 24 distillate is primarily due to the conversion from the free base to sulphate form prior to testing.

The difference in the XAD4 isotherms can be mainly attributed to distillate pH. In general, the solubility of a solute in water is frequently indicative of the ability of non-polar resins to adsorb that solute from an aqueous system. The solubility of phenol (and correspondingly, its degree of dissociation) increases with increasing pH and thus the XAD capacity for phenol would be expected

Figure 4.4 - WA30 Equilibrium Isotherms

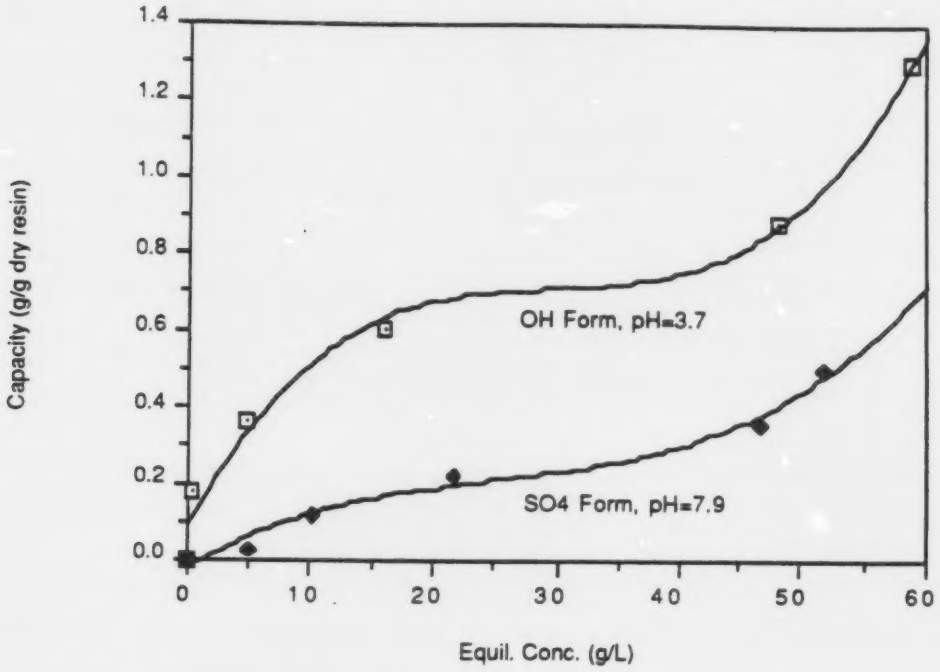
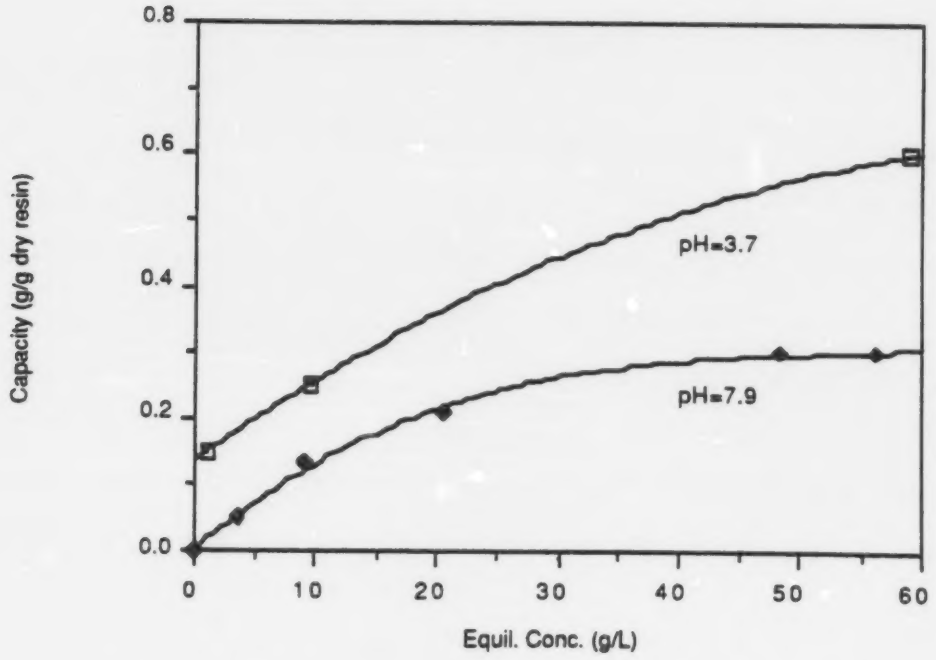


Figure 4.5 - pH Effect on XAD4 Capacity



to decrease. This trend was observed in the experimental results. The pH effect over the same range was negligible for the XAD7 resin.

4.3.3 Column Test

Initial column tests were carried out with WA30 and XAD7 resins to select the better performing resin. In each test, the resin beds were regenerated after a first loading and then loaded a second time. Four bed volumes of distillate effluent were collected during each loading step. Two bed volumes of 40% formaldehyde solution were used to elute phenol from the resin beds in the regeneration step. The experimental data obtained for each resin are given in Appendix II.

Mass balances were calculated for each step of the process to determine the relative efficiencies of the resins. The results of the calculations are presented in Table 4.5. In the first loading step, 88.8% of the phenol in the distillate feed was adsorbed by the WA30 resin compared to 75.2% by the XAD7 resin. The results showed no significant differences in elution efficiencies between the two resins. However, in the second loading step, the amount of phenol adsorbed by the WA30 resin dropped by 4% compared to less than 1% with the XAD7 resin. The information gathered was insufficient to select the most effective resin for this application. Further column tests had to be conducted with both resins.

In tests 2 to 4, breakthrough profiles were obtained for the WA30 and XAD7 resins at distillate feed rates of 2,4 and 6 BV/h. These profiles are shown in figures 4.6 and 4.7 respectively. Refer to Table 4.3 for the operating conditions under which the tests were conducted.

With the WA30 resin, the breakthrough profiles got sharper

Table 4.5 - Results of Column Screening Tests

Step	Resin Type	Mass Adsorbed (g)	% Phenol Loaded	% Phenol Eluted
1st Loading	XAD7	9.4	75.2	-
Regeneration	XAD7	-1.3	-	13.9
2nd Loading	XAD7	9.3	74.4	-
1st Loading	WA30	11.1	88.8	-
Regeneration	WA30	-1.6	-	14.2
2nd Loading	WA30	10.6	84.8	-

Operating Conditions:

Distillate Flow Rate = 2 BV/h
Eluant Flow Rate = 2 BV/h
Bed Depth = 10 cm
Bed Volume = 49 mL

Figure 4.6 - WA30 Breakthrough Profiles

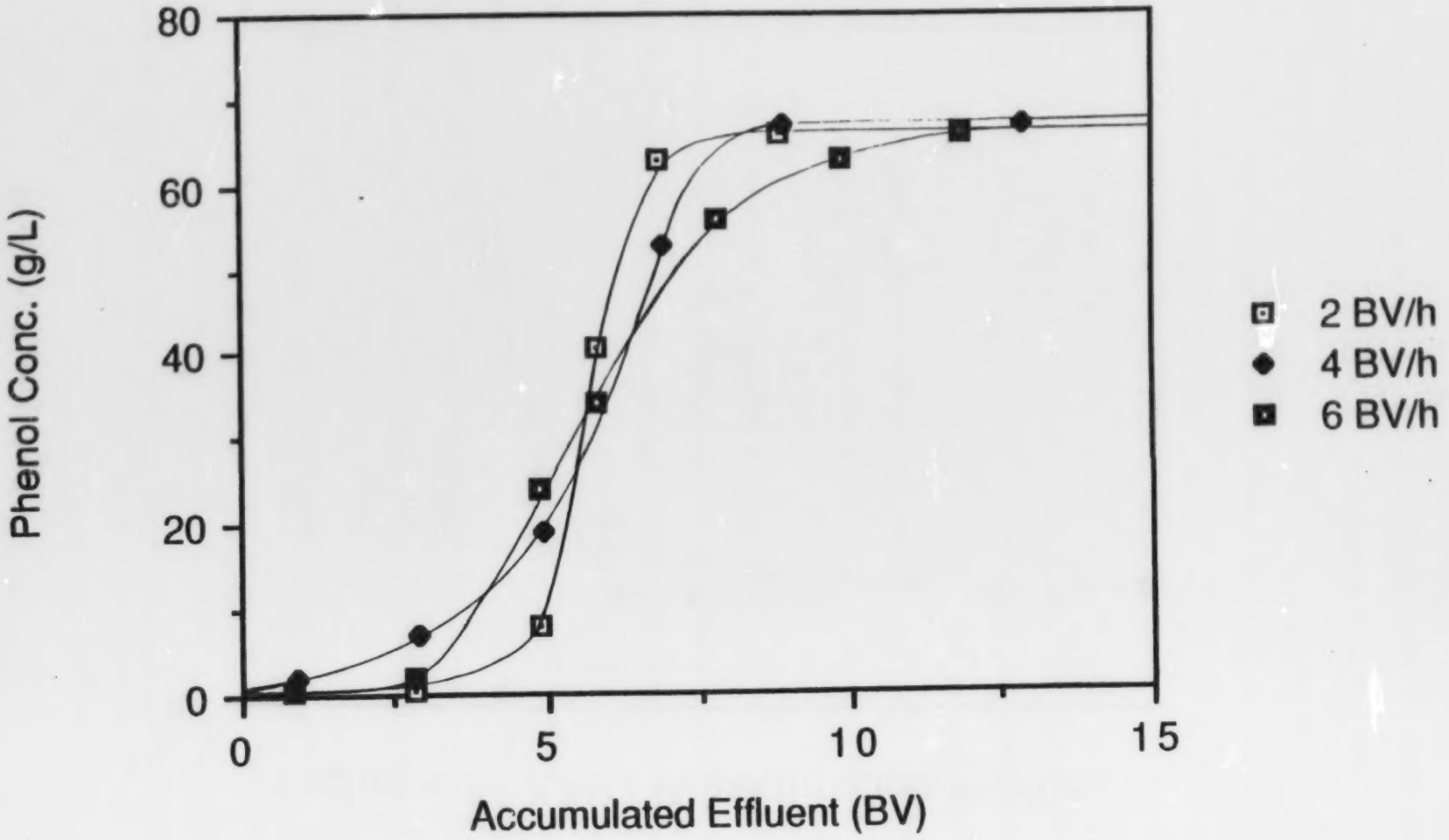
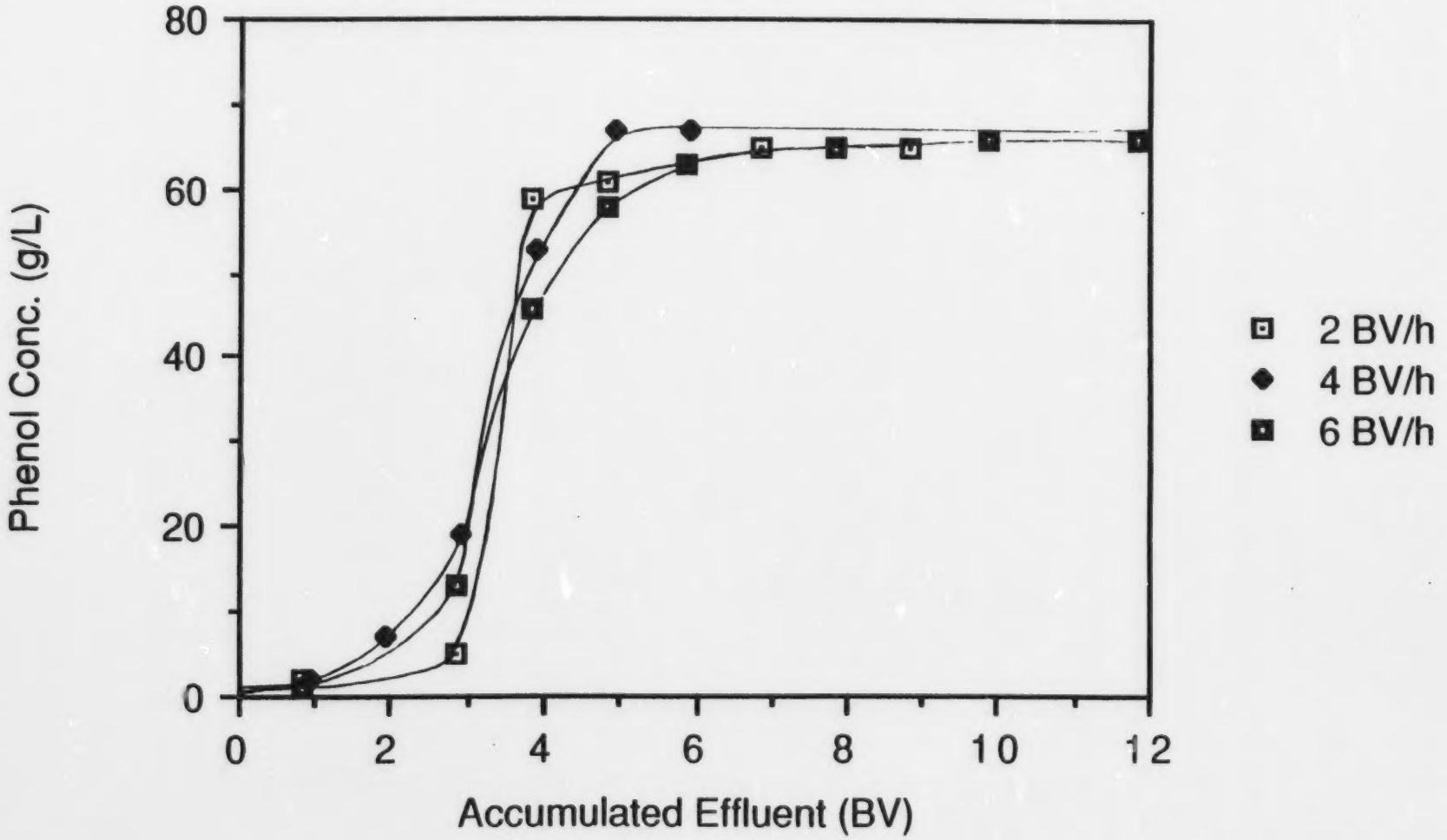


Figure 4.7 - XAD7 Breakthrough Profiles

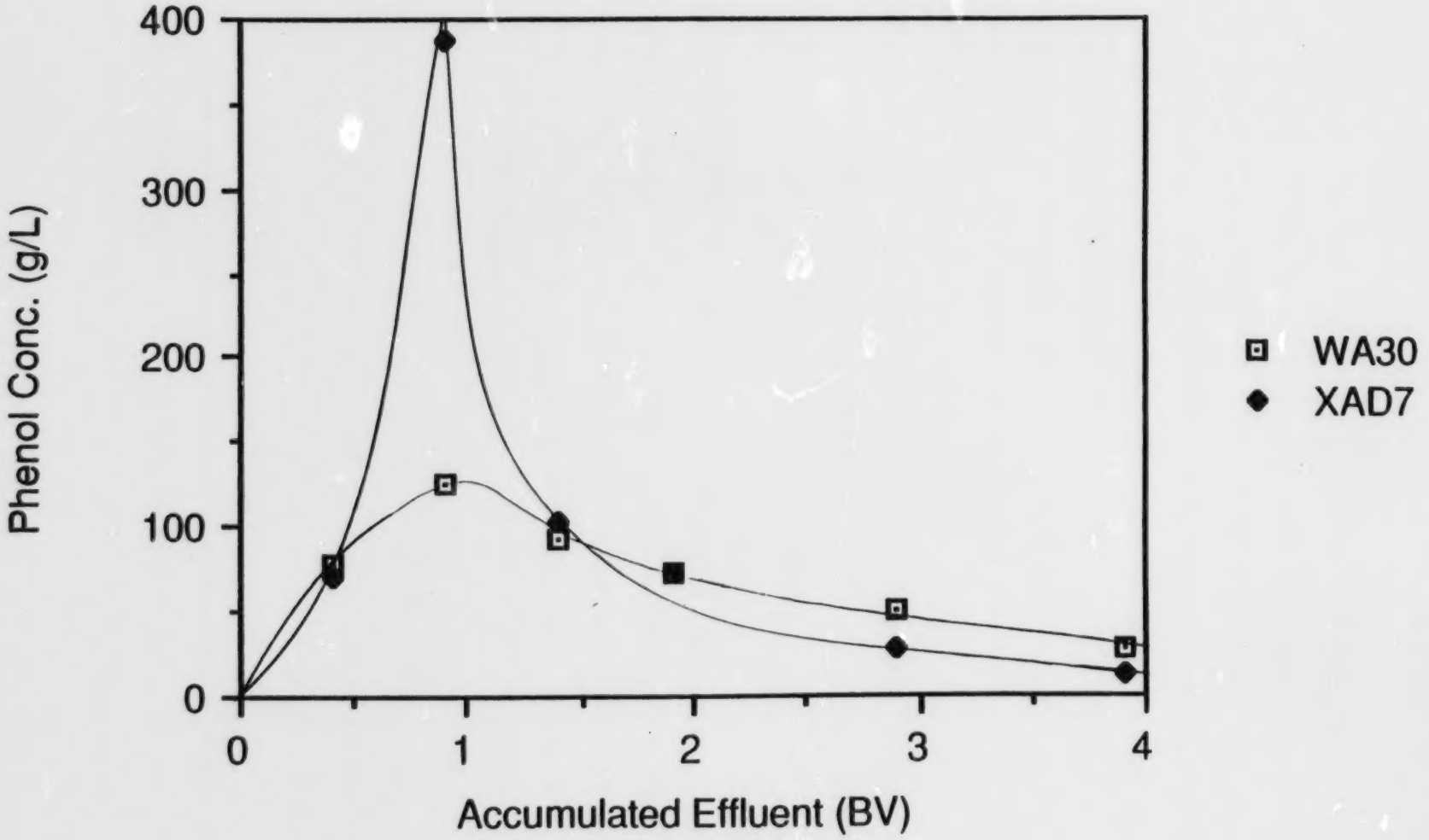


with decreasing feed flow rates. This trend was less evident with the XAD7 resin. The XAD7 profiles were in all cases sharper than the WA30 resin, and increasing feed flow rates were not observed to have a significant effect on the profile sharpness. Surface adsorption is a rapid process compared to ion exchange and hence the XAD7 is expected to adsorb phenol at a faster rate than WA30. The average pore diameter of the resin also governs adsorption kinetics if the process is primarily internally diffusion controlled (i.e. the greatest resistance to adsorption occurs in the transfer of solute from the exterior of the porous adsorbent to internal surface sites). No data could be obtained on the average pore diameter for the WA30 resin. Rohm and Haas reports an average pore diameter of 90 Angstroms for their XAD7 resin.

The sharpness of a breakthrough profile indicates the depth of the adsorption zone that moves through the column. Every adsorption operation has a critical minimum bed depth corresponding to the depth of the adsorption zone. Below this minimum depth, the concentration of solute in the effluent will rise sharply from the time the effluent is first discharged from the column. Hence, the sharpness of the profiles will have an effect on the height to diameter ratio and consequently the number of columns that will be required in a full-scale phenol recovery unit.

The operating capacity of the resin beds is another important design factor for sizing the full-scale unit. The WA30 and XAD7 resins were loaded to 50% of their total capacity after 5.7 and 3.6 BV respectively. The higher WA30 capacity corresponds to the

Figure 4.8 - Elution Profiles



higher equilibrium capacities observed in the equilibrium tests (see section 4.3.2).

In test 4, both resin beds were regenerated at 2 BV/h after the loading step. The elution profiles obtained are shown in figure 4.8. The XAD7 resin bed was regenerated more efficiently with 40% formaldehyde solution than the WA30 resin bed.

In summary, the experimental data gathered indicated advantages to using both the XAD7 and WA30 resins. The WA30 resin exhibited a significantly greater capacity for phenol both in equilibrium and column tests. However, the equilibrium tests proved that the WA30 capacity will be reduced after long-term column operation due to sulphate poisoning. On the other hand, the XAD7 resin regenerated more efficiently and maintained a fairly constant capacity after a second service cycle. Long term testing at a pilot-scale level is recommended before the most suitable resin can be selected for this application.

4.3.4 Design Calculations

A full-scale phenol recovery unit was sized for 8 hour/day operation. The unit consists of three columns, two on-line while the third is being regenerated. The following design criteria were made in sizing the full-scale unit:

Average distillate production = 11.8 L/min (1,500 gpd)

Distillate feed rate = 2 BV/h (2.5 cm3/min)

Eluant feed rate = 2 BV/h

Operating capacity = 90% of total capacity

Maximum phenol concentration in effluent = 5,000 mg/L

The design calculations are shown below:

Superficial velocity, u = Flow Rate (Q)/Cross-sectional area (A)

For the test column,

$$Q = 2 \text{ BV/h} = 2.5 \text{ cm}^3/\text{min}$$
$$A = 4.9 \text{ cm}^3$$

$$\text{therefore, } u = \frac{2.5 \text{ cm}^3/\text{min}}{4.9 \text{ cm}^3} = 0.5 \text{ cm/min}$$

For a full-scale column,

$$A = \frac{Q}{u} = 11{,}800 \frac{\text{cm}^3}{\text{min}} \times \frac{1}{0.5 \text{ cm/min}} = 23{,}600 \text{ cm}^2$$

therefore, Column diameter, D = 173 cm

From the WA30 and XAD7 breakthrough profiles, 90% of the resin bed capacity was exhausted after 7 and 4 BV respectively. At 2 BV/H, this corresponds to a service time of 3.5 hours for a WA30 resi bed and 2 hours for a XAD7 resin bed.

Therefore, using the WA30 resin,

Bed depth = 0.5 cm/min x 210 min = 105 cm

Column depth = 210 cm (for 100% bed expansion)

Using the XAD7 resin,

Bed depth = 0.5 cm/min x 120 min = 60 cm

Column depth = 102 cm (for 70% bed expansion)

It should be noted that, although the maximum phenol concentration in the effluent may reach as high as 5,000 mg/L, the average concentration of the treated effluent would be considerably less. Under the operating conditions outlined above, this average concentration was estimated to be between 2,000 and 3,000 mg/L.

5.0 ECONOMIC ANALYSIS

The main purpose of the bench-scale study was to obtain operating data that could be used in a preliminary (± 30%) economic assessment of the phenol recovery process. The results of the assessment would provide a basis for justifying further work on a pilot-scale level. Since the overall objective is both to recover phenol and to discharge the effluent to the sewerage system, a biological treatment plant is included as part of the distillate treatment process.

An economic analysis was performed based on an 8 hour per day, 5 day per week operation. The recovery process was sized to recover 90% of the distillate phenol with two columns operating in series. A third column is regenerated simultaneously and used to replace the next column that becomes exhausted.

The capital and operating costs for the proposed phenol recovery process is shown in Tables 5.1 and 5.2. Cost estimates were obtained for three instrumented adsorption columns (from IWT-Himsley). The estimate was based on a standard packaged unit with the column dimensions closest to those calculated in section 4.5. Auxiliary equipment consists of two stainless steel positive displacement pumps for pumping distillate and formaldehyde solution through the columns and the necessary piping for tying in the recovery unit to existing storage tanks. The resin cost was taken as the average cost for required WA30 and XAD7 bed volumes. An estimate of the installed cost for a biological treatment plant was obtained from CanadianOxy.

The net result of the economic analysis was an estimated

savings of $195,000/yr which corresponds to a payback period on investment of about 1.8 years. This result is very favourable and justifies further development and evaluation of the recovery process o a pilot-scale.

Table 5.1 - Capital Costs for Phenol Recovery Process

3 Instrumented adsorption columns (Epoxy-lined carbon steel with polypropylene-lined piping and fittings, fully automated)	$125,000
Auxiliary equipment (2 SS pumps and piping)	$5,000
Installation (20% of equipment costs)	$26,000
Resin (Average of 87 ft3 WA30 @ $210/ft3 and 50 ft3 XAD7 @ $333/ft3)	$17,500
Engineering (20% of capital costs)	$34,700
Biological Treatment Unit	$150,000
Total Capital Cost	**$358,000**

Table 5.2 - Operating Costs for Phenol Recovery Process

	($/yr)
Resin replacement (Based on 5-year life)	$3,500
Repairs and maintenance (3% of investment)	$10,700
Equipment Amortization (10 years, straight-line)	$30,600
Labour costs	$30,000
Total Operating Cost	$75,000
Credits:	
Recovered phenol (90% recovery @ $1.35/kg)	$110,000
Hauling and disposal cost (1,600 tonnes @ $100/1000 L)	$160,000
Net Savings	**$195,000**
Payback period	**1.8 years**

6.0 CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

- An initial techno-economic evaluation of existing phenol recovery technologies indicated that resin adsorption with formaldehyde regeneration was the only viable process for recovering phenol at the CanadianOxy plant.
- A bench-scale study confirmed the technical feasibility of the resin adsorption process and a preliminary economic analysis suggested that a payback period of 1.8 years is possible.
- Equilibrium adsorption tests showed that WA30, a weak base anion resin had the greatest capacity for phenol followed by XAD7, a slightly polar non-ionic adsorbent.
- Column tests again showed the greater capacity of the WA30 resin for adsorbing phenol, but the XAD7 resin was observed to regenerate more efficiently with 40% formaldehyde.
- The sharpness of the WA30 breakthrough profiles was affected more significantly by increasing the hydraulic loading from 2 to 6 BV/h than it was for the XAD7 profiles.

6.2 Recommendations

- Based on the favourable outcome of the bench-scale study, it is recommended that further process development and evaluation be carried out on a pilot-scale.
- Further testing will be required before the best performing resin can be selected for this application.
- The benefit of using Recoflo technology (i.e. short columns)

in this application should be assessed in the next phase of testing.

- A more detailed economic assessment of the phenol recovery process should be performed before a full-scale unit is constructed.

6.3 Proposed Work Plan for Phase 2 (Pilot Study)

The general objective of the Phase 2 work will be to set-up a pilot scale test unit to confirm the technical and economic suitability of the resin adsorption process for phenol recovery under actual plant operating conditions. On-site testing will also provide the necessary data for the design of the full-scale recovery system and assess the long-term reliability and flexibility of the process. A preliminary work plan for the pilot study was drafted based on three months of on-site testing and a budget of about $50,000. The proposed work plan is outlined below:

Task 1 - Design, Construction and Installation of Pilot-Scale Test Unit

In this task, a test unit suitably sized for direct scale-up will be designed and assembled in-house. The unit will consist of two or more columns with the required piping and instrumentation for safe, unattended operation and compatibility with existing process equipment ZENON will work closely with plant personnel in the scheduling and implementation of the pilot test program.

Task 2 - Column Testing and Process Optimization

The primary objective of this task is to perform column tests to verify the resin capacities and elution efficiencies observed for the XAD7 and WA30 resins in bench-scale tests. The best performing resin will be selected, and additional tests will be conducted to determine the optimum hydraulic loading, operating temperature, column configuration and phenol concentration cut-offs for the loading and regeneration steps.

Task 3 - Long-term Column Operation

Pilot-scale column operation will be conducted for a minimum of 3 months to establish the reliability of the resin adsorption recovery process under typical plant conditions. The data gathered will indicate the rate at which the resin loses its capacity for adsorbing phenol due to poisoning and/or resin deterioration. The operating experience will also allow better estimations of manpower and maintenance costs to be made.

Task 4 - Report Preparation

At the completion of Phase 2 work, a report will be prepared that summarizes the outcome of the pilot study and presents a detailed economic analysis of the phenol recovery process. The necessary design information for construction and installation of the full-scale system will also be included in the report.

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Appendix I

Experimental Data for Equilibrium Tests

WA-30 (OH Form)

Equil. Conc. (g/L)	Equil. Phenol (g)	Initial Phenol (g)	Resin Volume (L)	Resin Capacity (g/L dry resin)	Resin Capacity (g/g dry resin)	pH
59	5.9	9	0.005	620	1.30	4.87
48	4.8	9	0.01	420	0.88	5.45
16	1.6	4.5	0.01	290	0.61	5.71
4.7	0.47	2.25	0.01	178	0.37	6.52
0.3	0.03	0.9	0.01	87	0.18	6.88
36	3.6	6.38	0.01	278	0.58	7.15

WA-30 (SO4 Form)

Equil. Conc. (g/L)	Equil. Phenol (g)	Initial Phenol (g)	Resin Volume (L)	Resin Capacity (g/L dry resin)	Resin Capacity (g/g dry resin)	pH
52	5.2	6.38	0.005	236	0.49	4.51
47	4.7	6.38	0.01	168	0.35	2.75
22	2.2	3.19	0.01	99	0.21	2.17
10	1	1.595	0.01	59	0.12	2.09
5	0.5	0.638	0.01	14	0.03	2.01

HP-20

Equil. Conc. (g/L)	Equil. Phenol (g)	Initial Phenol (g)	Resin Volume (L)	Resin Capacity (g/L dry resin)	Resin Capacity (g/g dry resin)	pH
77	7.7	9	0.005	260	0.55	3.69
64	6.4	9	0.01	260	0.55	3.69
31	3.1	4.5	0.01	140	0.30	3.72
12	1.2	2.25	0.01	105	0.22	3.78
3.3	0.33	0.9	0.01	57	0.12	3.98
53	5.3	6.38	0.01	108	0.23	8.02

XAD-7

Equil. Conc. (g/L)	Equil. Phenol (g)	Initial Phenol (g)	Resin Volume (L)	Resin Capacity (g/L dry resin)	Resin Capacity (g/g dry resin)	pH
71	7.1	9	0.005	380	0.90	3.72
59	5.9	9	0.01	310	0.73	3.75
31	3.1	4.5	0.01	140	0.33	3.84
12	1.2	2.25	0.01	105	0.25	4.02
2	0.2	0.9	0.01	70	0.17	4.3
43	4.3	6.38	0.01	208	0.49	8.09

XAD-4

Equil. Conc. (g/L)	Equil. Phenol (g)	Initial Phenol (g)	Resin Volume (L)	Resin Capacity (g/L dry resin)	Resin Capacity (g/g dry resin)	pH
85	8.5	9	0.005	100	0.19	3.7
59	5.9	9	0.01	310	0.60	3.7
43	4.3	4.5	0.01	20	0.04	3.75
9.5	0.95	2.25	0.01	130	0.25	3.86
1	0.1	0.9	0.01	80	0.15	4.16
56	5.6	6.38	0.005	156	0.30	8
48	4.8	6.38	0.01	158	0.30	8.03
21	2.1	3.19	0.01	109	0.21	8.02
9	0.9	1.595	0.01	69	0.13	8.02
3.6	0.36	0.638	0.01	28	0.05	8.07

Appendix II

Experimental Data for Column Tests

TEST # 1

Operating Conditions:

Distillate Flow Rate = 2BV/h
Eluant Flow Rate = 2 BV/h
Bed Depth = 10 cm
Bed Volume = 49 mL
Sample Volume (Loading) = 2 BV (98 mL)
Sample Volume (Elution) = 1 BV (49 mL)

Experimental Data:

Sample # (Resin/BV)	Phenol Conc. (g/L)	Accumulated Vol. (mL)	Accumulated Vol. (BV)
Feed	64	0	0
	*** 1st Loading ***		
WA30/2	7.4	49	1
WA30/4	7.6	147	3
XAD7/2	6	49	1
XAD7/4	26	147	3
	*** Elution ***		
WA30/1	14	25	0.5
WA30/2	18	74	1.5
XAD7/1	13	25	0.5
XAD7/2	14	74	1.5
	*** 2nd Loading ***		
WA30/2	8.6	49	1
WA30/4	11	147	3
XAD7/2	6.2	49	1
XAD7/4	27	147	3

TEST # 2

Operating Conditions:

Distillate Flow Rate = 2 BV/h
Bed Depth = 15 cm
Bed Volume = 74 mL (in DI water)
Sample Volume = 25 mL

Experimental Data:

Sample # (Resin/BV)	Phenol Conc. (g/L)	Accumulated Vol. (mL)	Accumulated Vol. (BV)
Feed	68	0	0
WA30/1	0.3	62	0.84
WA30/3	0.3	210	2.84
WA30/5	8.3	358	4.84
WA30/6	41	432	5.84
WA30/7	63	506	6.84
WA30/9	66	654	8.84
XAD7/1	2.2	62	0.84
XAD7/3	5.1	210	2.84
XAD7/4	59	284	3.84
XAD7/5	61	358	4.84
XAD7/7	65	506	6.84
XAD7/9	65	654	8.84

TEST# 3

Operating Conditions:

Distillate Flow Rate = 4 BV/h
Bed Depth = 25 cm
Bed Volume = 123 mL
Sample Volume = 25 mL

Experimental Data:

Sample # (Resin/BV)	Phenol Conc. (g/L)	Accumulated Vol. (mL)	Accumulated Vol. (BV)
Feed	68	0	0
WA30/1	1.9	112	0.91
WA30/3	7	358	2.91
WA30/5	19	604	4.91
WA30/7	53	850	6.91
WA30/9	67	1096	8.91
WA30/13	67	1588	12.91
XAD7/1	1.6	112	0.91
XAD7/2	1.9	235	1.91
XAD7/3	15	358	2.91
XAD7/4	46	481	3.91
XAD7/5	60	604	4.91
XAD7/6	63	727	5.91

TEST # 4

Operating Conditions:

Distillate Flow Rate = 6 BV/h
Eluant Flow Rate = 2 BV/h
Bed Depth = 15 cm
Bed Volume = 74 mL (in DI water)
Loading Step Sample Volume = 25 mL
Regeneration Step Sample Voulme = 10 mL

Experimental Conditions:

Sample # (Resin/BV)	Phenol Conc. (g/L)	Accumulated Vol. (mL)	Accumulated Vol. (BV)
Feed	68	0	0
		*** Loading Step ***	
WA30/1	0.3	62	0.84
WA30/3	1.8	210	2.84
WA30/5	24	358	4.84
WA30/6	34	432	5.84
WA30/8	56	580	7.84
WA30/10	63	728	9.84
WA30/12	66	876	11.84
XAD7/1	1	62	0.84
XAD7/3	13	210	2.84
XAD7/4	46	284	3.84
XAD7/5	58	358	4.84
XAD7/6	63	432	5.84
XAD7/8	65	580	7.84
XAD7/10	66	728	9.84
XAD7/12	66	876	11.84

TEST # 4 (Cont'd)

Experimental Data:

Sample # (Resin/BV)	Phenol Conc. (g/L)	Accumulated Vol. (mL)	Accumulated Vol. (BV)
	*** Regeneration Step ***		
WA30/0.5	79	33	0.45
WA30/1	125	69	0.93
WA30/1.5	92	107	1.45
WA30/2	73	139	1.88
WA30/3	51	217	2.93
WA30/4	28	291	3.93
XAD7/0.5	70	33	0.45
XAD7/1	388	69	0.93
XAD7/1.5	104	107	1.45
XAD7/2	74	139	1.88
XAD7/3	27	217	2.93
XAD7/4	12	291	3.93